

times with C.P. ether. The extract was washed, dried and evaporated. The total crude benzoic acid weighed 4.78 g. (95%). A sample of this acid was recrystallized (Norit) from water, then sublimed *in vacuo* prior to assay, m.p. 121.5–122.5°; combustion water, % D₂O, 35.1.

Deuterated Benzamide.—The above deuterated benzoic acid (4.06 g.) was converted to benzamide by refluxing with thionyl chloride, followed by treatment of the residue therefrom with chilled ammonium hydroxide. The crude amide was recovered in 1.60 g. (40%) yield. It was recrystallized from a mixture of ethanol (1 ml./g.) and ligroin (3 ml./g.) to yield two crops: (1) 1.26 g., m.p. 126–127° and (2) 0.25 g., m.p. 121–123.5°.

Hofmann Degradation of Diluted Deuterated Benzamide.—1.487 g. of the above deuterated benzamide was diluted with 1.487 g. of recrystallized stock benzamide. The mixture was treated with a solution of potassium hydroxide (4.2 g.) and bromine (1.42 ml.) in water (38 ml.). The mixture was swirled thoroughly, then treated with a solution of potassium hydroxide (5.9 g.) in water (10 ml.). The temperature was maintained at 70–80° for 35 minutes, whereupon the mixture was steam distilled, collecting 75 ml. of distillate. The distillate was salted and extracted four times with ether. The extract was dried over potassium hydroxide, filtered and freed of solvent through a small column. The residue was 2.24 g. (98%) of crude aniline.

Deuterated Tribromoaniline.—Bromine (0.5 ml.) in acetic acid (3 ml.) and water (2 ml.) was added with stirring to 0.3 ml. of the above aniline dissolved in a mixture of acetic acid (2 ml.) and water (3 ml.). After five minutes the mixture was diluted with water, and the crude tribromoaniline (0.95 g., 89%) was collected. The latter was recrystallized twice (Norit) from dilute ethanol, to give 0.29 g. of a sample having m.p. 119.5–120°; combustion water, % D₂O, 13.1; corrected for dilution, 26.2%.

Deuterated Acetanilide.—One and nine-tenths grams of the above aniline was converted to acetanilide by the method described by Fieser.⁸ The crude product was obtained in 1.13 g. (41%) yield. A sample was purified by vacuum sublimation prior to deuterium assay, m.p. 113.5–114.5°; combustion water, % D₂O, 13.5, 12.5; corrected for dilution, 26.0%.

Deuterated *p*-Bromoacetanilide.—One gram of the above acetanilide was brominated according to the procedure of Fieser,⁹ using proportional reagent quantities. The crude product, 1.51 g. (95%), was recrystallized twice from dilute ethanol prior to deuterium assay, m.p. 167–167.5°; combustion water, % D₂O, 10.2; corrected for dilution, 20.4%.

Action of Deuterated Raney Nickel on Benzene.—About 4 g. of the above sample B deuterated Raney nickel was sucked damp-dry and treated with 40 ml. of azeotropically dried benzene. The mixture was distilled to a small volume, then treated with additional benzene and distilled to a residual volume of about 10 ml. At this point the clumped catalyst had become evenly dispersed through the solvent, no more D₂O was apparent in the distillate and the catalyst

was quite pyrophoric. The mixture was refluxed during 30 hr., then filtered damp-dry. The residual catalyst was markedly pyrophoric. Odor and infrared examination of the filtrate suggested the presence of a product other than benzene. Evaporation of 5.38 g. of the filtrate left a pasty residue of 0.07 g. (1.3%). This smelled like biphenyl and was purified twice by sublimation at 70° (0.5 mm.). The white sublimate had m.p. 69–70° and showed no mixed m.p. depression with a sublimed sample of biphenyl (m.p. 69–70°). In another experiment 2.40 g. of the above filtrate left 0.08 g. (3.7%) of crude biphenyl. This was purified by sublimation and combusted for deuterium assay; combustion water, % D₂O, 2.3.

A 0.25-ml. sample of the above benzene filtrate was freed of its deuterated biphenyl by passage through a 4-foot Celite-Silicone vapor phase chromatographic column.¹⁰ The benzene fraction was collected¹⁰ and combusted for deuterium assay; combustion water, % D₂O, 2.3.

Deuterated Raney Nickel in Benzene on Phenylacetamide.—A portion of sample B deuterated Raney nickel above was sucked damp-dry (25 g.). The damp sample was added to azeotropically topped benzene (300 ml.), and the mixture was distilled down to 60 ml., driving off the majority of residual D₂O and giving a uniform suspension of catalyst. Phenylacetamide (6.00 g.) and dry benzene (10 ml.) were added, and the mixture was refluxed for 18 hr. under CaCl₂-tube protection. The hot mixture was filtered and the cake was rinsed twice with boiling benzene and five times with boiling acetone. Solvent evaporation left 5.40 g. (90%) of product. A portion thereof was recrystallized twice from an ethanol-ligroin mixture, m.p. 157–158°; combustion water, % D₂O, 3.1.

In a separate experiment it was found that ordinary Raney nickel in benzene had no readily detectable chemical action on phenylacetamide during 65 hr. of refluxing.

Hydrolysis and Oxidation of Deuterated Phenylacetamide.—A 5.20-g. portion of the above deuterated phenylacetamide was hydrolyzed as before with refluxing 10% sodium hydroxide solution (100 ml.), then oxidized by treatment with excess potassium permanganate. Usual processing led to 4.11 g. (87.5%) of benzoic acid. A portion was recrystallized from water and sublimed prior to deuterium assay; combustion water, % D₂O, 2.5.

Deuterated Raney Nickel in Benzene on L(+)-Mandelamide.—Deuterated Raney nickel (sample B, 23 g. damp weight) was treated with dry benzene (200 ml.). The mixture was azeotropically dried by distillation to a volume of 60 ml., then treated with 1.00 g. of L(+)-mandelamide ($[\alpha]_D^{25} + 69.0^\circ$ (*c* 2, acetone), 96% optically pure). The mixture was refluxed for 5.2 hr., and the product (0.40 g.) was isolated as usual. It was dissolved in ethanol, and the solution was allowed to stand 18 hr., then evaporated to dryness. Two recrystallizations (Norit) from a mixture of ethanol and ligroin produced phenylacetamide having m.p. 157.5–158° and showing no optical activity beyond experimental error in acetone solution (*c* 3).

(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 165.

(9) Reference 8, p. 167.

(10) W. A. Bonner and T. W. Greenlee, THIS JOURNAL, **79**, 1696 (1957).

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, KYOTO UNIVERSITY]

The Dipole Moments and Molecular Structures of *ac-trans*-Dihalogetetralins¹

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The dipole moments of 2,3-dihalogetetralins and 1,2-dihalogetetralins were measured in solution at various conditions, to show that each of these compounds has a half-chair ring and can occur in two conformations which are in equilibrium through ring conversion. Then, the energy difference ΔE between the two conformations of each compound is estimated. From comparison of the ΔE values, it is concluded that the properties of 2,3-dihalogetetralins are very similar to those of corresponding dihalogenocyclohexenes, and the *aa* conformation of the 1,2-isomers is more stable than that of the 2,3-isomers.

The concept of "non-bonded energy"² in cyclo-

(1) Presented at the monthly meeting of Kansai Branch of the Agricultural Chemical Society of Japan, Kyoto, June 23, 1956.

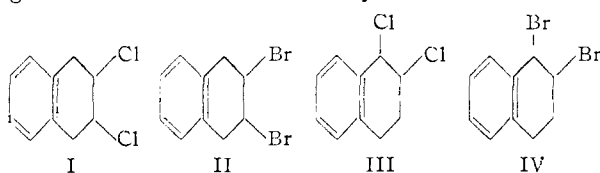
hexane derivatives has given clear explanations to

(2) W. Klyne, "Progress in Stereochemistry," Vol. 1, W. Klyne, Ed., Butterworths Scientific Pub., London, 1954, p. 36.

the stereostructures of polycyclic perhydro-systems, especially those of the steroids, and has been generally considered to be applicable to the partially unsaturated polycyclic compounds involving the cyclohexene or tetralin systems.³ It has been concluded by several investigators⁴⁻⁶ that, as in the case of cyclohexane derivatives, cyclohexene derivatives also are more stable in the half-chair form than in the half-boat form and can occur in two conformations which are in equilibrium through ring conversion, unless the energy difference between the two is too large.

If the small difference between the double bond lengths of cyclohexene and tetralin be neglected, quite similar arguments may be applied in these two systems. There has been, however, relatively little experimental evidence about the stereostructures of tetralin derivatives other than the X-ray analysis by Lasheen,⁷ who has shown that naphthalene tetrachloride has a half-chair ring.

In the work herein reported, dipole moments of four dihalogenotetralins (I-IV) were measured at various conditions to shed more light on the stereostructures of tetralin derivatives, especially that of 1,2,3,4-tetrahydro-1-naphthoic acid, a synthetic plant growth substance,⁸ which has been investigated in the author's laboratory.



Experimental

Preparation of Materials.⁹ **2,3-Dihalogenotetralins (I) and (II).**—To a solution of 10 g. (0.077 mole) of 1,4-dihydronaphthalene,¹⁰ b.p. 89–92° (20 mm.), in 50 ml. of carbon tetrachloride, 50 ml. of carbon tetrachloride containing 5.5 g. (0.078 mole) of chlorine or 12.5 g. (0.078 mole) of bromine was dropped slowly with stirring at 0°. The solvent was removed *in vacuo*, and the residue was recrystallized several times from ethanol to give 8 g. of I, m.p. 83.5–84° (reported¹¹ 84–85°), or 15 g. of II, m.p. 73–73.5° (reported 71.5–72°,¹⁰ 73.5–74°),¹² respectively.

1,2-Dihalogenotetralins (III) and (IV) were prepared by halogen addition to 1,2-dihydronaphthalene,^{10,13} b.p. 90° (20 mm.), in a procedure similar to that used in preparing the 2,3-isomers. From 3 g. of 1,2-dihydronaphthalene, there was obtained 2.5 g. of III, m.p. 40–41°. *Anal.* Calcd. for C₁₀H₁₀Cl₂: Cl, 35.28. Found: Cl, 35.43. Braun and Kirschbaum¹³ prepared liquid 1,2-dichlorotetralin, b.p. 155–160° (20 mm.), by direct chlorination of tetralin at 100°, and reported that this substance did not crystallize on cooling. It seems likely that this liquid was a mixture of *cis*- and *trans*-isomers.

(3) D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954).

(4) C. W. Beckett, N. K. Freeman and K. S. Pitzer, *THIS JOURNAL*, **70**, 4227 (1948).

(5) R. A. Pasternak, *Acta Cryst.*, **4**, 316 (1951).

(6) K. Sakashita, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **74**, 315 (1953).

(7) M. A. Lasheen, *Acta Cryst.*, **5**, 593 (1952).

(8) T. Mitsui and A. Tamura, *J. Agr. Chem. Soc. Japan*, **25**, 17 (1951).

(9) All temperature measurements are not corrected. A part of the preparation is by Mr. K. Shimazaki and microanalysis by Mr. H. Sato.

(10) F. Straus and L. Lemmel, *Ber.*, **46**, 232 (1913).

(11) E. Waser, *ibid.*, **49**, 1207 (1916).

(12) E. Bamberger and W. Lodter, *ibid.*, **20**, 1705 (1887).

(13) J. v. Braun and G. Kirschbaum, *ibid.*, **54**, 597 (1921).

In a similar manner, 5 g. of IV was obtained, m.p. 71–72° (reported 70–71°,¹⁰ 70°¹³).

Solvents.—Benzene, freed from thiophene by treatment with anhydrous aluminum chloride, was dried over metallic sodium and then distilled, and the fraction boiling at 80–80.5° was collected. *n*-Heptane was treated with concd. sulfuric acid, dried over metallic sodium and then distilled, and the fraction boiling at 95.5–98° was collected.

Measurement.—The dielectric constant ϵ of the solution was measured with the heterodyne beat apparatus as described by Morino and Miyagawa.¹⁴ The density d was determined with a pycnometer similar to that designed by Lipkin, Davison, Harvey and Kurtz.¹⁵ The total molar polarization $P_{2\infty}$ was calculated by a modified Hedestrand method similar to that introduced by Halverstadt and Kumler,¹⁶ differing in that densities were used rather than specific volumes

$$P_{2\infty} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \frac{M_2}{d_1} \left[1 + \frac{3a}{(\epsilon_1 - 1)(\epsilon_1 + 2)} - \frac{b}{d_1} \right]$$

where M_2 is molecular weight of solute, ϵ_1 and d_1 are, respectively, the dielectric constant and density of the solvent, and a and b are the coefficient of linear expansion of ϵ and d of solution with respect to the weight fraction of the solute w : $\epsilon = \epsilon_1 + aw$, $d = d_1 + bw$. The dipole moment μ is given by the equation

$$\mu = 0.0128 \{ [P_{2\infty} - (P_E + P_A)] T \}^{1/2}$$

where P_E and P_A are the electronic and atomic polarization of the solute, respectively, and T is the temperature in absolute scale. $P_E + P_A$ was taken to be equal to the molecular refraction calculated from the atomic refractions given in the Landolt-Börnstein table. The values thus obtained are listed in Table I. The experimental error in μ is $\pm 0.02 D$ in I and III and $\pm 0.03 D$ in II and IV.

TABLE I
RESULTS OF MEASUREMENTS

Solvent	T , °K.	ϵ_1	d_1	a	b	$P_{2\infty}$, cc.	μ , D	
I, 2,3-Dichlorotetralin: $P_E + P_A = 52.23$ cc.								
Benzene	283	2.3037	0.8890	1.658	0.271	108.33	1.61	
	298	2.2731	.8729	1.630	.271	108.97	1.60	
	313	2.2435	.8571	1.602	.270	109.66	1.72	
<i>n</i> -Heptane	274	1.9803	.7322	1.167	.321	98.53	1.44	
	298	1.9457	.7117	1.178	.322	101.17	1.55	
	323	1.9093	.6899	1.140	.321	101.43	1.61	
II, 2,3-Dibromotetralin: $P_E + P_A = 58.03$ cc.								
Benzene	298	2.2730	0.8727	0.645	0.441	84.19	1.13	
	313	2.2434	.8569	.661	.448	84.58	1.17	
	274	1.9814	.7324	.533	.447	78.00	0.95	
<i>n</i> -Heptane	298	1.9469	.7118	.540	.435	80.38	1.04	
	323	1.9096	.6903	.550	.432	81.92	1.12	
	III, 1,2-Dichlorotetralin: $P_E + P_A = 52.23$ cc.							
Benzene	298	2.2730	0.8729	1.390	0.279	99.26	1.52	
	274	1.9810	.7326	1.125	.324	96.13	1.40	
	298	1.9464	.7121	1.097	.318	97.10	1.48	
<i>n</i> -Heptane	323	1.9088	.6903	1.072	.320	97.60	1.55	
	IV, 1,2-Dibromotetralin: $P_E + P_A = 58.03$ cc.							
	Benzene	298	2.2733	0.8726	0.847	0.443	95.00	1.34
274		1.9801	.7325	.790	.442	97.71	1.34	
298		1.9455	.7120	.740	.442	95.10	1.35	
<i>n</i> -Heptane	323	1.9091	.6903	.677	.433	92.51	1.35	

Discussion

An appropriate model of the tetralin molecule is required for the analysis of the moment values obtained. First, the half-chair model will be discussed. It is assumed that unsaturated and allylic carbon atoms are coplanar, and the intramolecular distortions are minimum when the bond distances

(14) Y. Morino and I. Miyagawa, *Kagaku-no-Ryohiki (J. Japan. Chemistry)*, Extra No. 8 (1953).

(15) M. R. Lipkin, J. A. Davison, W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

(16) L. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

and bond angles in Fig. 1 are taken as follows: C=C, 1.38 Å.; C—C, 1.54 Å.; $\angle\theta = 122^\circ$, $\angle\gamma = 111^\circ 04'$, $\angle\delta = 108^\circ$, $\angle\beta = \angle\beta' = 109^\circ 28'$, $\angle\alpha = 109^\circ 50'$, $\angle\alpha' = 109^\circ 04'$. To calculate the dipole moments, (i) as the moment value of tetralin itself, 0.52 *D* in benzene obtained by Sidgwick and Springall¹⁷ is used, and (ii) the empirical rule suggested by Morino, Miyagawa and Oiwa¹⁸ is applied, which is as follows: (1) C → Cl, C → Br and C → H bond moments are assumed to be 1.86, 1.79¹⁹ and 0.00 *D*, respectively. (2) In the C—C bond in which C atom locates in the α -position to the first halogen atom, a moment of 0.27 *D* (hal. = Cl) or 0.51 *D* (hal. = Br) is induced in the direction of C ← C. (3) In the C—C bond in which C atom locates in the β -position to the first halogen atom, a moment of 0.15 *D* is induced in the direction of C ← C. (4) In the C—halogen bond in which C atom locates in the β -position to the first halogen atom, a moment of 0.24 *D* (hal. = Cl) or 0.42 *D* (hal. = Br) is induced in the direction of C ← halogen.

The calculation by this rule, instead of using 1.91 *D* for C—halogen bond moment,²⁰ seems reasonably accurate because of the good agreement of observed and calculated moment values of a number of halogenated hydrocarbons, especially polyhalogenocyclohexanes.^{18,21}

In III and IV, this rule cannot be directly applied; therefore, the double bond in the benzene ring is regarded to be a single bond. This assumption may be quite adequate, because the induction effect estimated from this assumption is nearly equivalent to that from the moment values of benzyl halide and methyl halide.

TABLE II

DIPOLE MOMENTS CALCULATED FROM MOLECULAR MODEL^a

	<i>cis</i>		<i>trans</i>	
	<i>ae</i>	<i>ea</i>	<i>aa</i>	<i>ee</i>
I, 2,3-Dichloro-	2.70	2.70	0.09	3.15
II, 2,3-Dibromo-	2.57	2.57	.51	3.10
III, 1,2-Dichloro-	3.13	3.28	.96	3.24
IV, 1,2-Dibromo-	3.01	3.08	1.32	3.26

^a Symbols *a* and *e* are used as in cyclohexane derivatives; *a*, nearer to the perpendicular of the benzene ring; *e*, nearer to the plane of the benzene ring than the other.

The moments thus calculated for different conformations of each geometrical isomer are shown in Table II. From this table it is clear that if these compounds are of *trans* configurations, the apparent average moment values should vary with the abundance ratio of two conformations at a given temperature unless the energy difference ΔE between them is too large, because the calculated moment values

(17) N. V. Sidgwick and H. D. Springall, *J. Chem. Soc.*, 1532 (1936).

(18) Y. Morino, I. Miyagawa and T. Oiwa, *Botyu-Kagaku (Scientific Insect Control)*, **15**, 181 (1950); I. Miyagawa, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 1061 (1954).

(19) These are the observed moment values for methyl chloride and methyl bromide in the gaseous state; cf. S. Sanger, O. Steiger and K. Gachter, *Helv. Phys. Acta*, **5**, 200 (1932); L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937).

(20) A. Tulinski, A. DiGiacomo and C. P. Smyth, *THIS JOURNAL*, **75**, 3552 (1953); P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3462 (1955).

(21) I. Miyagawa, Y. Morino and R. Riemschneider, *Bull. Chem. Soc. Japan*, **27**, 177 (1954); T. Shimozawa, Y. Morino and R. Riemschneider, *ibid.*, **28**, 393 (1955).

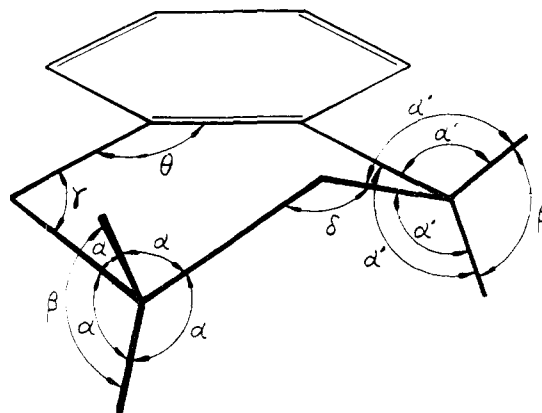


Fig. 1.

undergo appreciable change through ring conversion. On the other hand, if these are of *cis* configurations, their moment values should be observed in the neighborhood of 2.5–3.0 *D* relatively independent of the temperature. But actually, as shown in Table I, the observed values are found around 1.6 *D* (I), 1.1 *D* (II), 1.5 *D* (III) and 1.3 *D* (IV), and apparent moments of I, II and III increase with temperature. Therefore, it is concluded that these four compounds are of *trans* configurations and that the addition of halogen to dihydronaphthalene proceeds as a *trans* addition.

The more stable conformation of I, II or III is obviously *aa*. In IV, $d\mu/dT \cong 0$. If the energy difference ΔE between two conformations were equal to zero, then the apparent moment value should become 1.8 *D* independently of temperature. Because the observed moment values 1.35 *D* are in good agreement with the calculated value for the *aa* conformation, 1.32 *D*, IV exists almost entirely as the *aa* conformation.

Let the number of the *aa* molecules be N_a and that of the *ee* molecules be N_e , then the following equation is obtained; $N_e/N_a = e^{-\Delta E/RT}$, and the apparent dipole moment $\bar{\mu}$ is calculated as

$$\bar{\mu}^2 = \frac{N_e \mu_e^2 + N_a \mu_a^2}{N_e + N_a} = \frac{\mu_a^2 + \mu_e^2 \exp(-\Delta E/RT)}{1 + \exp(-\Delta E/RT)}, \text{ or}$$

$$\bar{\mu}^2 - \mu_a^2 = \frac{\mu_e^2 - \mu_a^2}{1 + \exp(\Delta E/RT)}$$

where μ_a and μ_e are the theoretical moment values of *aa* and *ee* conformations, respectively. Using the apparent moment values $\bar{\mu}$ observed at different temperatures and the calculated moment values μ_a in Table II, the energy differences ΔE and the moments μ_e of the *ee* conformations are calculated for I, II and III, according to the method proposed by Lennard-Jones and Pike.²² The lower limit of ΔE of IV is obtained from the equation²³

$$4\Delta\mu \cdot \bar{\mu} \geq (\mu_e^2 - \mu_a^2) [1/\{1 + \exp(\Delta E/RT)\} - 1/\{1 + \exp(\Delta E/RT')\}]$$

where $\Delta\mu$ is the experimental error, T and T' are the highest and lowest temperatures at which the moments are measured. In this equation, $\Delta\mu$, $\bar{\mu}$, μ_a and μ_e are taken to be 0.03, 1.35, 1.32 and 3.22 *D*,

(22) J. E. Lennard-Jones and H. M. Pike, *Trans. Faraday Soc.*, **30**, 845 (1934).

(23) I. Miyagawa, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 1162 (1954).

respectively. The results thus obtained are shown in Table III. Even if the values of μ_a of II and IV are taken to be equal to the values of chloro analogs I and III, respectively, the results do not undergo an appreciable change.

TABLE III
ENERGY DIFFERENCE BETWEEN TWO CONFORMATIONS

Solvent	ΔE , cal./mole	μ_a , D	μ_a (D) calcd. from model	
I	Benzene	800 \pm 150	3.6 \pm 0.3	3.15
	<i>n</i> -Heptane	900 \pm 150		
II	Benzene	1400 \pm 200	3.5 \pm 0.3	3.10
	<i>n</i> -Heptane	1550 \pm 200		
III	<i>n</i> -Heptane	1350 \pm 150	3.7 \pm 0.4	3.24
IV	<i>n</i> -Heptane	\geq 2000	3.26

As discussed above, the half-chair model can well explain the observed moment values. On the other hand, the model of the half-boat form cannot, because the calculated moment values become considerably larger than the observed values, e.g., in the compound I, *cis* form, $2e3e$ (3.3 D) \rightleftharpoons $2a3a$ (3.5 D); *trans* form, $2a3e = 2e3a$ (2.2 D). Recently, Kumler and Huitric²⁴ have demonstrated that "six-membered ring compounds with two or more atoms in the ring that do not have sp^3 -binding, such as a bivalent atom or a carbonyl which has essentially sp^2 -binding, are most likely to have flexible forms" from the study of the molecular structures of α -halocyclohexanones. These dihalogenotetralins are such a type of compound since the ring with halogens has two carbon atoms with sp^2 -binding. Even if the observed facts can well be explained by the half-chair model, it is too much to decide only from dipole moment values that these dihalogenotetralins have the half-chair structure and have not any contributions from the half-boat or the other flexible structures. The fact that compounds I, II and III have different moments in benzene and *n*-heptane and that the moments in any one solvent vary with temperature, may be accounted for by the alternative hypothesis that a flexible form makes an appreciable contribution to the structure, according to Kumler and Huitric's idea.

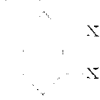
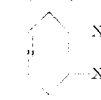
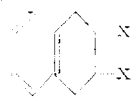
However, taking into consideration Sakashita's results,⁶ from Raman spectra of *trans*-4,5-dichloro-1-cyclohexene, that this compound has only two possible structures in the liquid state or solution, and from the dipole moment values, that the observed facts can well be explained only when these two possible structures are the *aa* and *ee* conformations of the half-chair structure, it is quite reasonable to conclude that these tetralin derivatives, structurally very similar compounds to dichlorocyclohexene, are also of half-chair ring structure.

The fact that ΔE of II or IV is, respectively, larger than that of I or III in the same solvent, may be caused by the larger van der Waals radius of the bromine atom, as in the case of dihalogenocyclohexanes and -cyclohexenes.

The structural chemical properties of 2,3-dihalogentetralins are very similar to those of the corresponding dihalogenocyclohexenes, as shown in Ta-

ble IV. It seems that in these substances, where a condensed benzene ring is compared with a double bond, there are no remarkable differences in the properties, as the various interactions about halogen atoms opposite to a double bond or a benzene ring are nearly the same. The change of ΔE with solvent may be explained as in the case of the rotational isomers of 1,2-dihalogenoethanes,²⁵ in which the energy difference decreases with the increasing dielectric constant of the solvent.

TABLE IV
 ΔE VALUES (CAL./MOLE) OF I AND II, AND THEIR RELATED COMPOUNDS IN VARIOUS SOLVENTS

X	Solvent			
Cl	C ₆ H ₆	-400 ^a	700 ^b	800
	<i>n</i> -C ₇ H ₁₆	900
	CCl ₄	50 ^a	800 ^b	..
Br	C ₆ H ₆	80 ^a	1300 ^c	1400
	<i>n</i> -C ₇ H ₁₆	500 ^a	..	1550
	CCl ₄	500 ^a	1400 ^c	..

^a K. Kozina, K. Sakashita and S. Maeda, THIS JOURNAL, 76, 1965 (1954). ^b Ref. 6. ^c K. Sakashita, private communication, April, 1956.

The increase of ΔE from dihalogenocyclohexanes to -cyclohexenes or -tetralins is supposed to be caused partly by the following factor. In these compounds, the *aa* conformation is subjected to the mutual repulsion between hydrogen and halogen atoms which are in so-called *meta-axial* relationship. In dihalogenocyclohexane, there are 4 *meta-axial* pairs in *aa* conformation, but in dihalogenocyclohexene and -tetralin, owing to the disappearance of two hydrogen atoms, there are only 2 *meta-axial* pairs. Therefore, it seems that *aa* forms of the latter two are less subjected to such repulsion than the former, so *aa* forms of dihalogenocyclohexene and -tetralin are more stable than that of dihalogenocyclohexane.

It is clear from Table III that ΔE values of 1,2-dihalogentetralins are considerably larger than those of the corresponding 2,3-dihalogentetralins. The bonds attached to C-1 are not truly equatorial or axial in character, and the directions of these bonds are less distinguishable than those attached to C-2, but the interactions of halogen atom at C-1 with C-8 and H at C-8 do not exist in the 2,3-isomers, and it is considered that these interactions play an important role in the increase of ΔE . Then, it is reasonable to consider that in 1,2-dihalogentetralin, both halogen-H at C-8 and halogen-C-8 distances are considerably shorter in *ee* than in *aa*, therefore, the steric repulsion in *ee* of 1,2-dihalogentetralin becomes greater than in that of the 2,3-isomer, making the former considerably more unstable than the latter.

From the discussions above, the following conclusions are obtained: (1) Each of these *ac-trans*-dihalogentetralins has a half-chair ring and can occur in two conformations through ring conversion, as in the case of dihalogeno-cyclohexane and cyclohexene. (2) The structural chemical prop-

(24) W. D. Kumler and A. C. Huitric, THIS JOURNAL, 78, 4599 (1954).

(25) A. Wada, J. Chem. Phys., 22, 158 (1954).

erties of *trans*-2,3-dihalogenotetralin are very similar to those of *trans*-4,5-dihalogeno-1-cyclohexene. (3) As to *trans*-1,2-dihalogenotetralin, probably because of the sterical repulsions of halogen at C-1 with C-8 and H at C-8, the *ee* conformation become more unstable than that of the 2,3-isomer, therefore, ΔE becomes larger than that of 2,3-dihalogenotetralin.

From these conclusions the following could be speculated: (1) In regard to *ac*-monosubstituted positional isomers, the abundance ratio of *axial* conformation to *equatorial* one may become larger in α -substituted tetralin than in the β -substituted one. (2) In 1,2-disubstituted tetralin, not only of *trans* configuration but of *cis* configuration, the more stable conformation may be generally the

one in which the substituent at C-1 is *axial*. When two substituents are fused together to make another ring, the *trans* configuration cannot occur other than in *1e2e*; in the *cis* configuration, however, *1a2e* may be more stable than *1e2a*.

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Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide. VI. Hexaphenylethane¹

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The effects of solute purity, light and oxygen on the electrical conductivity of sulfur dioxide solutions of hexaphenylethane have been investigated. Contrary to previous reports, pure solutions of hexaphenylethane do not conduct significantly. Electrolytes are, however, generated by the action of light and of oxygen. Comparison of the data for oxygenated solutions of hexaphenylethane with the conductivity of tetramethylammonium sulfate in liquid sulfur dioxide at 0.1° over the dilution range 200 to 100,000 liters per mole suggests that a 2-1 electrolyte is present. These observations make possible simple explanation of earlier reports on the properties of solutions of hexaarylethanes in sulfur dioxide.

Introduction

The differences in behavior of solutions of hexaphenylethane² in sulfur dioxide and in organic solvents has been the subject of considerable discussion. Thus in so called "non-ionizing" solvents, molecular weight,³ magnetic susceptibility⁴ and spectral⁵ data in conjunction with photochemical instability⁶ and rapid reaction with oxygen⁷ demonstrate conclusively the dissociation of hexaarylethanes into free radicals. In sulfur dioxide, however, the solutions have been reported to conduct the electric current,⁸ to be photochemically stable⁹ and to fail to react with oxygen.¹⁰ Moreover, the observed color¹¹ and spectrum¹² in SO₂ have been de-

scribed as differing markedly from those observed in many other solvents.¹³

This anomalous behavior has received several chemical interpretations¹⁴ which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and sulfur dioxide. These proposed mechanisms can be divided into two general classes depending upon the valence type of the electrolyte produced and, therefore, in view of the recent demonstration¹⁵ of the applicability of modern electrolyte theory to solutions of electrolytes in sulfur dioxide, would be distinguishable on the basis of conductivity data alone. Unfortunately the data of Walden^{8a} and of Gomberg^{8b} lack precision and do not extend over a sufficient concentration range to be useful for this purpose. Accordingly, attempts were made initially to obtain precise conductivity data employing crystalline samples of pure hexaphenylethane. These investigations revealed¹⁶ that the observed conductivity is an artifact of interaction with light or oxygen and is not characteristic of pure solutions.

(1) Based on a dissertation submitted by H. P. Leftin in partial fulfillment of a requirement for the Ph.D. at Boston University, May, 1955.

(2) For general reviews of this subject see: (a) M. Gomberg, *Chem. Revs.*, **1**, 91 (1924); (b) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 680-713.

(3) (a) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2037 (1904); (b) M. Gomberg and C. S. Schoepfle, *THIS JOURNAL*, **39**, 1652 (1917).

(4) (a) N. W. Taylor, *ibid.*, **48**, 854 (1926); (b) E. Muller, I. Muller-Radloff and W. Bunge, *Ann.*, **520**, 235 (1935); (c) M. F. Roy and C. S. Marvel, *THIS JOURNAL*, **59**, 2622 (1937); (d) R. Preckel and P. W. Selwood, *ibid.*, **63**, 3397 (1941).

(5) (a) J. Piccard, *Ann.*, **381**, 347 (1911); (b) K. Ziegler and L. Ewald, *ibid.*, **473**, 163 (1929).

(6) S. T. Bowden and W. J. Jones, *J. Chem. Soc.*, 1149 (1928).

(7) (a) M. Gomberg, *Ber.*, **33**, 3150 (1900); *THIS JOURNAL*, **22**, 757 (1900); (b) J. Schmidlin, *Ber.*, **41**, 2471 (1908).

(8) (a) P. Walden, *Z. physik. Chem.*, **43**, 443 (1903); (b) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2033 (1904); **38**, 1342 (1905); (c) M. Gomberg and F. W. Sullivan, Jr., *THIS JOURNAL*, **44**, 1810 (1922).

(9) Reference 6, p. 1153.

(10) L. C. Anderson, *THIS JOURNAL*, **57**, 1673 (1935).

(11) M. Gomberg and F. W. Sullivan, *ibid.*, **44**, 1829 (1922).

(12) (a) K. H. Meyer and H. Wieland, *Ber.*, **44**, 2557 (1911); (b) Reference 10.

(13) Ziegler and Ewald, reference 5b, reported that the spectra of hexaphenylethane solutions are identical in a series of solvents covering a wide range of dielectric constant, ion solvating power and structural properties.

(14) (a) Reference 2a, p. 102; (b) P. Walden, "Chemie der Freien Radicale," S. Hirzel, Leipzig, 1924, p. 154; (c) W. A. Waters, "Chemistry of Free Radicals," Oxford Press, London, 1948, pp. 35-36; (d) Reference 2b, p. 712; (e) H. I. Cole, *Philippine J. Sci.*, **19**, 681 (1922); (f) G. Cilento and W. F. Walter, *THIS JOURNAL*, **76**, 4469 (1954).

(15) (a) N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5530 (1951); (b) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160, 164 (1956).

(16) H. P. Leftin and N. N. Lichtin, *THIS JOURNAL*, **76**, 2593 (1954).